

PATENT ABSTRACTS OF JAPAN

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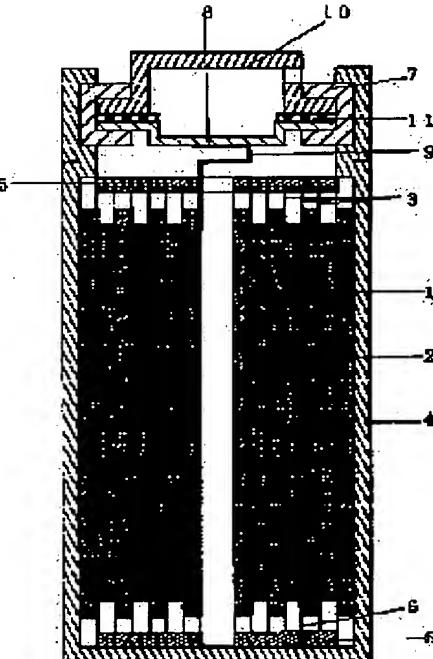
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(54) SECONDARY BATTERY

(57)Abstract:

PURPOSE: To largely supplement the capacity deterioration caused by charge/ discharge cycles by adding and mixing one oxide selected among BaO, MgO, and CaO to a lithium containing composite oxide, and generating the positive electrode of a lithium ion secondary battery.

CONSTITUTION: MnO₂ and Li₂CO₃ are mixed at the atomic ratio of 1:2 between Li and Mn, and the mixture is baked in the air at 800° C for 20hrs to obtain LiMn₂O₄, for example. One or more of 2 pts.wt. selected among BaO, MgO, and CaO and graphite of 8 pts.wt. are added to LiMn₂O₄ of 87 pts.wt. for example, for wet blending, and polyvinylidene fluoride of 3 pts.wt. as a binder and N-methyl-2-pyrrolidone as a solvent are added to obtain slurry by wet blending. This slurry is uniformly applied on both faces of an aluminum foil having the thickness of 0.02mm, for example, and serving as a positive electrode current collector, and it is pressed and molded by a roller press machine after drying to obtain a band-like positive electrode 2. A porous polypropylene separator 3 is sandwiched between a negative electrode 1 and the positive electrode 2, and they are wound into a roll shape to form a battery element.



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CLAIMS

[Claim(s)]

[Claim 1] The nonaqueous electrolyte rechargeable battery characterized by coming to add one or more sorts of oxides which mix with said active material and are chosen from BaO, MgO, and CaO into a positive electrode in the nonaqueous electrolyte rechargeable battery with which it is the cell which has a positive electrode, a negative electrode, a separator, and nonaqueous electrolyte, and a lithium content multiple oxide is used for said positive electrode as an active material.

[Claim 2] The nonaqueous electrolyte rechargeable battery according to claim 1 which uses a lithium manganese multiple oxide (for example, LiMn₂O₄) as positive active material.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the engine-performance improvement of a nonaqueous electrolyte rechargeable battery.

[0002]

[Description of the Prior Art] While miniaturization of electronic equipment and lightweight-ization are advanced, the request of the rechargeable battery of a high energy consistency has become strong further as the power source. In order to reply to the request, the nonaqueous electrolyte rechargeable battery attracted attention and the utilization has been tried. although the so-called lithium secondary battery which uses a lithium metal especially for a negative

electrode was considered for possibility to be the largest, in order that the engine performance deteriorates remarkably, and it may powder-ize by the repeat of charge and discharge, a metal lithium may deposit in a dendrite and a metal lithium negative electrode may cause internal short-circuit, a problem is in a practical cycle life and it is now -- utilization is difficult. So, recently, the nonaqueous electrolyte rechargeable battery which uses the carbon electrode using receipts and payments of the lithium ion to carbon as a negative electrode is developing. This cell was named the rechargeable lithium-ion battery, was begun in 1990, was introduced to the world by this invention person etc., and by current, it is recognized, so that it is called a next-generation rechargeable battery "a rechargeable lithium-ion battery" also at the cell industry and a society (9 magazine Progress In Batteries & SolarCells, Vol. 1990p 209), and it has required the spur for that utilization. A lithium content multiple oxide (for example, LiMn_2O_4 , LiCoO_2 , LiNiO_2 grade) is typically used for a positive-electrode ingredient, and carbonaceous ingredients, such as corks and graphite, are used for a negative electrode. Actually LiCoO_2 is used for a positive electrode, a special carbon material (pseudo-graphite ingredient with a certain amount of random layer structure) is used for a negative electrode, and little practical use of the rechargeable lithium-ion battery with the energy density like 200 Wh/l has already been carried out. The energy density of the existing nickel-cadmium battery is 100 – 150 Wh/l, and the energy density of a rechargeable lithium-ion battery easily exceeds it of the existing cell. However, it is that a material cost is quite high as a big fault. When considering a cheap rechargeable lithium-ion battery, since [like a resource], a price fall of cobalt cannot be desired in the future. Therefore, in respect of a cheap ingredient, a lithium manganese multiple oxide (LiMn_2O_4 , LiMnO_2 grade) is very attractive as a positive-electrode ingredient of a rechargeable lithium-ion battery. Furthermore, another fault of a rechargeable lithium-ion battery is that degradation of the capacity accompanying a charge-and-discharge cycle is large. And the degradation is remarkably large what used the lithium manganese multiple oxide as a positive-electrode ingredient. Since, as for a carbon negative electrode, the carbon to a lithium ion is only dedoped by discharge by doping a lithium ion in charge to the carbon in an electrode and carbon itself is not accompanied by change of the big crystal structure on the occasion of charge and discharge, the charge-and-discharge property stabilized extremely is shown, there is little property degradation accompanying charge and discharge, and the repeat of 1000 times or more of charges and discharges is also specifically possible. However, degradation of the capacity accompanying the cycle of an actual rechargeable lithium-ion battery is governed by property degradation of a positive electrode, and cannot be said to be sufficiently satisfactory level.

[0003]

[Problem(s) to be Solved by the Invention] This invention relates to an improvement of the cycle property of the nonaqueous electrolyte rechargeable battery which uses a lithium content multiple oxide as a main positive-active-material ingredient.

[0004]

[Means for Solving the Problem] The means of technical-problem solution comes to add one or more sorts of oxides which mix with the lithium content multiple oxide which is positive active material, and are chosen from BaO , MgO , and CaO into a positive electrode.

[0005]

[Function] If a lithium content multiple oxide (LiMn_2O_4 , LiMnO_2 and LiCoO_2 , LiNiO_2 grade) is used for a positive electrode, in the state of charge, a lithium ion will be in the condition of having been dedoped, and any multiple oxide will become unstable. Therefore, since positive active material changes gradually while repeating charge and discharge repeatedly, and the charge-and-discharge function is lost gradually, capacity deteriorates in connection with the charge-and-discharge cycle. Then, this invention person used to find out that capacity degradation accompanying the increase of the stability of the positive active material of a charge condition and a charge-and-discharge cycle serves as a very small nonaqueous electrolyte rechargeable battery by mixing with positive active material one or more sorts of oxides chosen from BaO , MgO , and CaO , and adding in a positive electrode, as a result of inquiring wholeheartedly for the purpose of stabilization of the positive active material in a charge condition.

[0006]

[Example] Hereafter, an example explains this invention in more detail.

[0007] This invention is explained about a concrete cylindrical cell, referring to example 1 drawing 1 . Drawing 1 shows the whole cell structure of this example. The cell component which is a generation-of-electrical-energy element for carrying out this invention was prepared as follows. The polyvinylidene fluoride (PVDF) 10 weight section was added to 90 weight sections of the meso carbon micro bead (d002=3.37A) which heat-treated at 2800 degrees C as a binder, wet blending was carried out to the N-methyl-2-pyrrolidone which is a solvent, and it was made the slurry (the shape of a paste). And this slurry was applied to homogeneity to both sides of copper foil with a thickness of 0.01mm it is thin to a charge collector, pressurization molding was carried out with the roller press machine after desiccation, and the band-like negative electrode (1) was created. Then, the positive electrode was prepared as follows. A commercial manganese dioxide (MnO₂) and a commercial lithium carbonate (Li₂CO₃) were mixed so that the atomic ratio of Li and Mn might turn into a presentation ratio of 1:2, this was calcinated at 800 degrees C among air for 20 hours, and LiMn₂O₄ was adjusted. Eight weight sections may be added for the BaO₂ weight section and graphite to 87 weight sections of this LiMn₂O₄, it mixes, wet blending of the N-methyl-2-pyrrolidone which are the polyvinylidene fluoride 3 weight section and a solvent as a binder further is added and carried out, and it is made a slurry (the shape of a paste). This slurry was applied to homogeneity to both sides of aluminium foil with a thickness of 0.02mm it is thin to a positive-electrode charge collector, pressurization molding was carried out with the roller press machine after desiccation, and the band-like positive electrode (2) was created. In this way, the negative electrode (1) and positive electrode (2) which were created were wound up in the shape of a roll on both sides of the separator made from porosity polypropylene (3) in the meantime, and created the cell component as a winding object with an average outer diameter of 15.7mm. Next, an electric insulating plate (5) is installed in the pars basilaris ossis occipitalis of an iron cell can (4) which performed nickel plating, and the above-mentioned cell component is contained. The negative-electrode lead (6) taken out from the cell component is welded to the bottom of the above-mentioned cell can, and the mixed solution of ethylene carbonate (EC) and diethyl carbonate (DEC) which dissolved one mol [/l.] LiPF₆ into the cell can is poured in as the electrolytic solution. Then, an electric insulating plate (5) is installed also in the upper part of a cell component, a gasket (7) is inserted in, and an explosion-proof valve (8) is installed in the interior of a cell, as shown in drawing 1 . Before the positive-electrode lead (9) taken out from the cell component injects the electrolytic solution into this explosion-proof valve, it is welded. On the explosion-proof valve, the lock out lid (10) used as a positive-electrode external terminal was piled up on both sides of the doughnut mold PTC switch (11), and the cell (A) with an outer diameter [of 16.5mm] and a height of 65mm was completed with the cell structure which shows the edge of a cell can in drawing 1 in total.

[0008] Creating the positive electrode which carries out example use of a comparison with the conventional method, all others were made the same as an example 1, and created the cell (X) by the conventional method. The positive electrode by the conventional method is prepared as follows. Eight weight sections mixing of the graphite is carried out for the shape 2O₄ of end LiMn₂O₄ of complications adjusted in the example 1 at 89 weight sections, wet blending of the N-methyl-2-pyrrolidone which are the polyvinylidene fluoride 3 weight section and a solvent as a binder further is added and carried out, and it is made a slurry (the shape of a paste). Next, this slurry was applied to homogeneity to both sides of aluminium foil with a thickness of 0.02mm it is thin to a positive-electrode charge collector, pressurization molding was carried out with the roller press machine after desiccation, and the band-like positive electrode (2c) was created. The rest wound up the same negative electrode (1) as this positive electrode (2c) and the thing created in the example 1 in the shape of a roll on both sides of the separator made from porosity polypropylene (3) in the meantime, created the cell component with an average outer diameter of 15.7mm, after that, was made the same as an example 1, and completely created the cell (X).

[0009] Two weight sections of MgO and the graphite 8 weight section are mixed in 87 weight sections of having adjusted [LiMn₂O₄ / 2O₄] in the example 2 example 1, wet blending of the N-methyl-2-pyrrolidone which are the polyvinylidene fluoride 3 weight section and a solvent as a

binder further is added and carried out, and it is made a slurry (the shape of a paste). Then, this slurry was applied to homogeneity to both sides of aluminium foil with a thickness of 0.02mm it is thin to a positive-electrode charge collector, pressurization molding was carried out with the roller press machine after desiccation, and the band-like positive electrode (2b) was created. The rest wound up the same negative electrode (1) as this positive electrode (2b) and the thing created in the example 1 in the shape of a roll on both sides of the separator made from porosity polypropylene (3) in the meantime, created the cell component with an average outer diameter of 15.7mm, also after that, was made the same as an example 1, and completely created the cell (B).

[0010] a test result -- after making it pass the aging period of 12 hours in ordinary temperature for the purpose of the stabilization inside a cell, each cell created in examples 1 and 2 and the example of a comparison in this way set the charge upper limit electrical potential difference as 4.2V, performed charge of 8 hours in ordinary temperature, similarly performed discharge to termination electrical-potential-difference 3.0V by 800mA constant-current discharge about all cells in ordinary temperature, and calculated the initial discharge capacity of each cell. Each cell performed the charge-and-discharge cycle trial in the 40-degree C thermostat after that. The charging current is 400mA, and the charge upper limit electrical potential difference was set as 4.2V, charge of 4 hours was performed, and discharge went by 800mA constant-current discharge to termination electrical-potential-difference 3.0V, repeated charge and discharge, and calculated the discharge capacity in 800mA discharge of each cell in a 40 cycle and 100 cycle time. The result is as having collected into Table 1. Even if the cell (A) by this invention and (B) repeat charge and discharge, there are few the capacity falls, and the capacity difference with the cell (X) of the conventional method by the example of a comparison becomes quite large at each [which are 40 cycle and 100 cycle] time as shown in Table 1. Like the rechargeable lithium-ion battery created by this example, in using a lithium manganese multiple oxide (LiMn₂O₄) for positive active material, in the especially hot charge-and-discharge cycle, capacity becomes less quite rapidly so that the cell (X) created with the conventional method may see. At the 100 cycle time, it will already become the capacity like the one half of initial capacity.

第1表

	初期容量 mAh	40サイクル時点の容量 mAh	100サイクル時点の容量 mAh
電池 [A]	975	918	885
電池 [B]	954	898	880
電池 [X]	980	782	520

However, as shown in Table 1, also in the cell which used the lithium manganese multiple oxide (LiMn₂O₄) for the positive electrode as positive active material by the cell (A) by this invention which carried out addition mixing of BaO and the MgO, and (B), extremely, a degradation degree decreases and the discharge capacity of 880-885mAh is obtained also at the 100 cycle time. This will be about 230 Wh/l, if it is made into an energy density, and it also exceeds the initial energy density of the rechargeable lithium-ion battery which used the cobalt by which current commercialization is carried out. Moreover, in internal resistance change, it is at the 100 cycle termination time, and it was checked to change of the (X) dozens milli ohms being seen, as for the cell by the conventional method that internal resistance change of the cell by this invention has very little (A) and (B) at a number milli ohm. This invention can improve sharply capacity degradation accompanying the cycle which was the biggest fault of a rechargeable lithium-ion battery as mentioned above. In addition, although the above-mentioned example explained the case where LiMn₂O₄ was used as positive active material, as an example in which the effectiveness of this invention appears most notably, also in the nonaqueous electrolyte rechargeable battery which uses LiCoO₂ and the lithium content multiple oxide of LiNiO₂ grade others as positive active material, this invention expresses an improvement effect. Moreover, although the above-mentioned example explained the case where added BaO and MgO to positive active material, and a positive electrode was created, the addition effectiveness with

same CaO is shown.

[0011]

[Effect of the Invention] If it is in this invention as stated above, capacity degradation accompanying the charge-and-discharge cycle which is the old big fault of a rechargeable lithium-ion battery is sharply improvable by adding one or more sorts of oxide which is mixed to a lithium content multiple oxide (for example, LiMn_2O_4 , LiCoO_2 , LiNiO_2 grade), and is chosen from BaO , MgO , and CaO , and creating the positive electrode of a rechargeable lithium-ion battery. Being able to offer now especially the high capacity and the long lasting and cheap rechargeable lithium-ion battery which an improvement effect is remarkable in the rechargeable lithium-ion battery using a lithium manganese multiple oxide as positive active material, and can fully replace the existing rechargeable battery, the industrial value is size.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The typical sectional view having shown the structure of the cell in an example and the example of a comparison

[Description of Notations]

1 -- a negative electrode and 2 -- a positive electrode and 3 -- a separator and 4 -- for a negative-electrode lead and 7, as for an explosion-proof valve and 9, a gasket and 8 are [a cell can and 5 / an electric insulating plate and 6 / a negative-electrode lead and 10] lock out lids.

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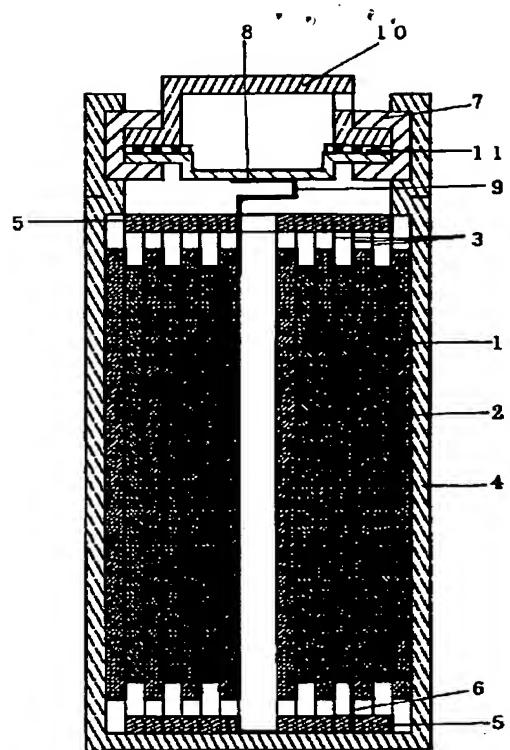
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DRAWINGS

[Drawing 1]



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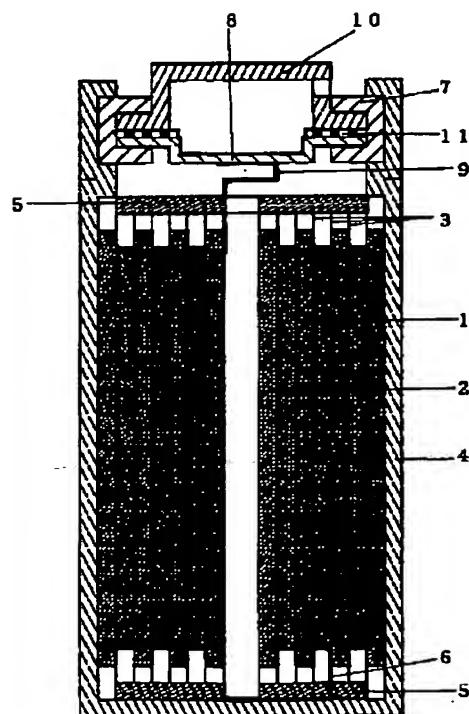
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(54)【発明の名称】 二次電池

(57)【要約】

【目的】 この発明は、非水電解液二次電池の性能改善に関するものである。

【構成】 リチウム含有複合酸化物（例えばLiMn₂O₄、LiCoO₂、LiNiO₂等）を正極活物質として用いる非水電解液二次電池において、正極にBaO、MgO、CaOから選ばれる1種以上の酸化物を添加混合することにより、充放電サイクルに伴う容量劣化が大幅に改善される。特に、リチウムマンガン複合酸化物を正極活物質とし、負極活物質としてX線広角回折法によるd002 (002面の面間隔)が3.42以下である黒鉛質材料を使用したリチウムイオン二次電池においては改善効果が著しく、既存の二次電池に充分代わる、高容量、長寿命で活安価なリチウムイオン二次電池が実現する。



【特許請求の範囲】

【請求項1】正極、負極、セパレータおよび非水電解液を有する電池であって、前記正極にはリチウム含有複合酸化物が活物質として使用される非水電解液二次電池において、正極中に前記活物質に混じてBaO、MgO、CaOから選ばれる1種以上の酸化物を添加してなることを特長とする非水電解液二次電池。

【請求項2】リチウムマンガン複合酸化物（例えばLiMn₂O₄）を正極活物質として使用する請求項1記載の非水電解液二次電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】この発明は、非水電解液二次電池の性能改善に関するものである。

【0002】

【従来の技術】電子機器の小型化、軽量化が進められる中、その電源として高エネルギー密度の二次電池の要望がさらに強まっている。その要望に答えるため、非水電解液二次電池が注目され、その実用化が試みられてきた。特に負極にリチウム金属を使用する、いわゆるリチウム二次電池は最も可能性が大きいと思われたが、金属リチウム負極は充放電の繰り返しによりパウダー化して著しくその性能が劣化したり、また金属リチウムがデンドライトに析出し内部ショートを引起したりするため、実用的なサイクル寿命に問題があり、今だ実用化は難しい。そこで最近ではカーボンへのリチウムイオンの出入りを利用するカーボン電極を負極とする非水電解液二次電池が開発中である。この電池は本発明者等によって、リチウムイオン二次電池と名付けて1990年に始めて世の中に紹介されたもので（雑誌Progress in Batteries & Solar Cells, Vol. 9, 1990, p209）、現在では電池業界、学会においても次世代の二次電池“リチウムイオン二次電池”と呼ばれるほどに認識され、その実用化に拍車がかかっている。代表的には正極材料にリチウム含有複合酸化物（例えばLiMn₂O₄、LiCoO₂、LiNiO₂等）を用い、負極にはコクスやグラファイト等の炭素質材料が用いられる。実際、正極にLiCoO₂を使用し、負極には特殊な炭素材料（ある程度の乱層構造を有した擬黒鉛材料）を使用して、200Wh/1程のエネルギー密度を持つリチウムイオン二次電池が既に少量実用されている。既存のニッケルカドミウム電池のエネルギー密度は100~150Wh/1であり、リチウムイオン二次電池のエネルギー密度は既存の電池のそれをはるかに上回るものである。しかしだ大きな欠点としてはかなり原材料費が高いことである。安価なリチウムイオン二次電池を考えるうえで、資源的な理由からコバルトの価格低下は将来においても望めない。したがって、安価な材料という点ではリチウムマンガン複合酸化物（LiMn₂O₄、LiMnO₂等）がリチウム

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ムイオン二次電池の正極材料としては極めて魅力的である。さらにリチウムイオン二次電池のもう一つの欠点は、充放電サイクルに伴う容量の劣化が大きいことである。しかも正極材料としてリチウムマンガン複合酸化物を使用したものではその劣化は著しく大きい。カーボン負極は、充電においては電極中のカーボンヘリチウムイオンがドープされ、放電ではそのカーボンからリチウムイオンが脱ドープされるだけで、カーボン自身は充放電に際して大きな結晶構造の変化を伴わないので、極めて安定した充放電特性を示し、充放電に伴う特性劣化が少なく、具体的には1000回以上の充放電の繰り返しも可能である。しかし、実際のリチウムイオン二次電池のサイクルに伴う容量の劣化は、正極の特性劣化により支配され、充分満足なレベルとは言えない。

【0003】

【発明が解決しようとする課題】本発明はリチウム含有複合酸化物を主たる正極活物質材料とする非水電解液二次電池のサイクル特性の改善に関するものである。

【0004】

【課題を解決するための手段】課題解決の手段は、正極中に正極活物質であるリチウム含有複合酸化物に混じてBaO、MgO、CaOから選ばれる1種以上の酸化物を添加してなるものである。

【0005】

【作用】正極にリチウム含有複合酸化物（LiMn₂O₄、LiMnO₂、LiCoO₂、LiNiO₂等）を使用すると、充電状態ではいずれの複合酸化物もリチウムイオンが脱ドープされた状態となり、不安定になる。従って充放電を何回も繰り返していくうち、正極活物質が徐々に変化し次第に充放電機能を失っていくため、充放電サイクルに伴って容量が劣化していく。そこで本発明者は充電状態にある正極活物質の安定化を目的に鋭意研究した結果、BaO、MgO、CaOから選ばれる1種以上の酸化物を正極活物質に混じて正極中に添加することにより、充電状態の正極活物質の安定性が増し、充放電サイクルに伴う容量劣化が緩和されることがわかった。非水電解液二次電池となることを見いだしたものである。

【0006】

【実施例】以下、実施例により本発明をさらに詳しく説明する。

【0007】実施例1

図1を参照しながら本発明を具体的な円筒型電池について説明する。図1は本実施例の電池の全体構造を示すものである。本発明を実施するための発電要素である電池素子は次のようにして用意した。280°Cで熱処理を施したメソカーボンマイクロビーズ（d002=3.37Å）の90重量部に接着剤としてポリフッ化ビニリデン（PVDF）10重量部を加え、溶剤であるN-メチル-2-ピロリドンと湿式混合してスラリー（ペースト状）にした。そしてこのスラリーを集電体となる厚さ

0.01 mmの銅箔の両面に均一に塗布し、乾燥後ローラープレス機で加圧成型して帯状の負極（1）を作成した。続いて正極は次のようにして用意した。市販の二酸化マンガン（MnO₂）と炭酸リチウム（Li₂CO₃）をLiとMnの原子比が1:2の組成比になるように混合し、これを空気中800°Cで20時間焼成してLiMn₂O₄を調整した。このLiMn₂O₄の87重量部にBaO2重量部、グラファイトを8重量部を加えてよく混合し、さらに結合剤としてポリフッ化ビニリデン3重量部と溶剤であるN-メチル-2-ピロリドンを加えて湿式混合してスラリー（ペースト状）にする。このスラリーを正極集電体となる厚さ0.02 mmのアルミニウム箔の両面に均一に塗布し、乾燥後ローラープレス機で加圧成型して帯状の正極（2）を作成した。こうして作成した負極（1）と正極（2）はその間に多孔質ポリプロピレン製セパレータ（3）を挟んでロール状に巻き上げて、平均外径15.7 mmの巻回体として電池素子を作成した。次にニッケルメッキを施した鉄製の電池缶（4）の底部に絶縁板（5）を設置し、上記電池素子を収納する。電池素子より取り出した負極リード

（6）を上記電池缶の底に溶接し、電池缶の中に1モル/リットルのLiPF₆を溶解したエチレンカーボネイト（EC）とジエチルカーボネート（DEC）の混合溶液を電解液として注入する。その後、電池素子の上部にも絶縁板（5）を設置し、ガスケット（7）を嵌め、防爆弁（8）を図1に示すように電池内部に設置する。電池素子より取り出した正極リード（9）はこの防爆弁に電解液を注入する前に溶接しておく。防爆弁の上には正極外部端子となる閉塞蓋体（10）をドーナツ型PTCスイッチ（11）を挟んで重ね、電池缶の縁をかじめて、図1に示す電池構造で外径16.5 mm、高さ6.5 mmの電池（A）を完成した。

【0008】比較例

使用する正極を従来法により作成し、他は全て実施例1と同じにして従来法による電池（X）を作成した。従来法による正極は次のようにして用意される。実施例1で調整した粉末状LiMn₂O₄を89重量部にグラファイトを8重量部混合し、さらに結合剤としてポリフッ化ビニリデン3重量部と溶剤であるN-メチル-2-ピロリドンを加えて湿式混合してスラリー（ペースト状）にする。次に、このスラリーを正極集電体となる厚さ0.02 mmのアルミニウム箔の両面に均一に塗布し、乾燥後ローラープレス機で加圧成型して帯状の正極（2c）

を作成した。後は、この正極（2c）と実施例1で作成したものと同じ負極（1）をその間に多孔質ポリプロピレン製セパレータ（3）を挟んでロール状に巻き上げて、平均外径15.7 mmの電池素子を作成し、全くその後は実施例1と同じにして電池（X）を作成した。

【0009】実施例2

実施例1で調整したのLiMn₂O₄の87重量部にMgOの2重量部、グラファイト8重量部を混合し、さらに結合剤としてポリフッ化ビニリデン3重量部と溶剤であるN-メチル-2-ピロリドンを加えて湿式混合してスラリー（ペースト状）にする。続いてこのスラリーを正極集電体となる厚さ0.02 mmのアルミニウム箔の両面に均一に塗布し、乾燥後ローラープレス機で加圧成型して帯状の正極（2b）を作成した。後は、この正極（2b）と実施例1で作成したものと同じ負極（1）をその間に多孔質ポリプロピレン製セパレータ（3）を挟んでロール状に巻き上げて、平均外径15.7 mmの電池素子を作成し、全くその後も実施例1と同じにして電池（B）を作成した。

【0010】テスト結果

こうして実施例1、2及び比較例で作成した電池は、いずれも電池内部の安定化を目的に常温で12時間のエージング期間を経過させた後、充電上限電圧を4.2 Vに設定し、常温で8時間の充電を行い、放電は同じく常温で全ての電池について800 mAの定電流放電にて終止電圧3.0 Vまで行い、それぞれの電池の初期放電容量を求めた。その後各電池は40°Cの高温槽中で充放電サイクル試験を行った。充電電流は400 mAで、充電上限電圧は4.2 Vに設定して4時間の充電を行い、放電は800 mAの定電流放電にて終止電圧3.0 Vまで行って充放電を繰り返し、40サイクルおよび100サイクル時点での各電池の800 mA放電での放電容量を求めた。その結果は表1にまとめた通りである。表1に示すとおり、本発明による電池（A）および（B）は充放電を繰り返しても、その容量低下が少なく、40サイクル、100サイクルの各時点では比較例による従来法の電池（X）との容量差はかなり大きくなる。本実施例で作成したリチウムイオン二次電池のように、正極活性質にリチウムマンガン複合酸化物（LiMn₂O₄）を使用する場合には、従来法で作成した電池（X）に見られるように、特に高温における充放電サイクルでは容量がかなり急激に減っていく。100サイクル時点ではすでに初期容量の半分程の容量となってしまう。

第1表

	初期容量 mA h	40サイクル時点の容量 mA h	100サイクル時点の容量 mA h
電池[A]	975	918	885
電池[B]	954	898	880
電池[X]	980	782	520

しかし表1に示すように、正極にBaOおよびMgOを添加混合した本発明による電池(A)および(B)では、正極活物質としてリチウムマンガン複合酸化物(LiMn₂O₄)を使用した電池においても、極めて劣化度合いは少なくなり、100サイクル時点でも880～885mA·hの放電容量が得られる。これはエネルギー密度にすれば約230Wh/1であり、現在商品化されているコバルトを使用したリチウムイオン二次電池の初期エネルギー密度をも上回るものである。また内部抵抗変化においては、100サイクル終了時点で、従来法による電池は(X)数十ミリオームの変化が見られるのに対し、本発明による電池の内部抵抗変化は(A)、(B)共に数ミリオームで非常に少ないと確認された。以上のように本発明はリチウムイオン二次電池の最も大きな欠点であったサイクルに伴う容量劣化を大幅に改善することが出来る。なお上述の実施例では本発明の効果がもっとも顕著に表れる例として、正極活物質としてLiMn₂O₄を使用した場合について説明したが、LiCoO₂やLiNiO₂等他のリチウム含有複合酸化物を正極活物質として使用する非水電解液二次電池においても本発明は改善効果を現すものである。また上述の実施例では正極活物質にBaOおよびMgOを添加し

て正極を作成した場合について説明したが、その他にもCaOが同様な添加効果を示す。

【0011】

【発明の効果】以上述べたように本発明にあっては、リチウム含有複合酸化物(例えばLiMn₂O₄、LiCoO₂、LiNiO₂等)に混合してBaO、MgO、CaOから選ばれる1種以上の酸化物を添加してリチウムイオン二次電池の正極を作成することにより、リチウムイオン二次電池のこれまでの大きな欠点である充放電サイクルに伴う容量劣化を大幅に改善できる。特に、リチウムマンガン複合酸化物を正極活物質として用いるリチウムイオン二次電池においては、改善効果が著しく、既存の二次電池に充分に代わりうる、高容量、長寿命で且つ安価なリチウムイオン二次電池を提供できるようになり、その工業的価値は大である。

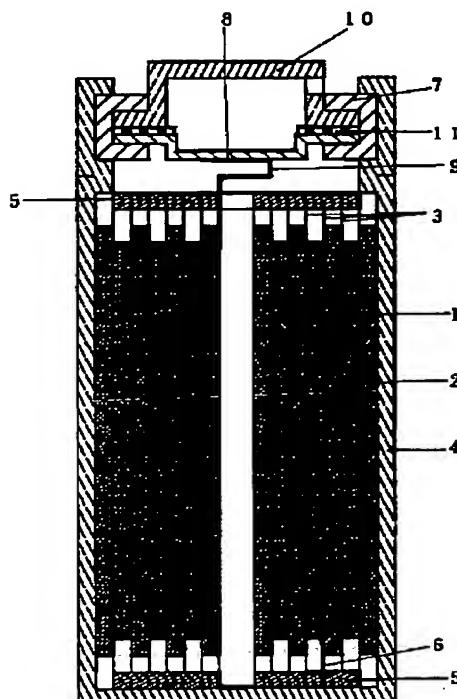
【図面の簡単な説明】

【図1】実施例および比較例における電池の構造を示した模式的断面図

【符号の説明】

1は負極、2は正極、3はセパレータ、4は電池缶、5は絶縁板、6は負極リード、7はガスケット、8は防爆弁、9は負極リード、10は閉塞蓋体である。

【図1】



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